

Orbital ordering in frustrated Jahn-Teller systems

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We consider the superexchange in ‘frustrated’ Jahn-Teller systems, such as the transition metal oxides NaNiO_2 , LiNiO_2 , and ZnMn_2O_4 , in which transition metal ions with doubly degenerate orbitals form a triangular or pyrochlore lattice and are connected by the 90° metal-oxygen-metal bonds. We show that this interaction is much different from a more familiar exchange in systems with the 180° -bonds, e.g. perovskites. In contrast to the strong interplay between the orbital and spin degrees of freedom in perovskites, in the 90° -exchange systems spins and orbitals are decoupled: the spin exchange is much weaker than the orbital one and it is ferromagnetic for all orbital states. Due to frustration, the mean-field orbital ground state is strongly degenerate. Quantum orbital fluctuations select particular ferro-orbital states, such as the one observed in NaNiO_2 . We also discuss why LiNiO_2 may still behave as an orbital liquid.

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There is a large class of compounds containing transition metal (TM) ions with orbital degeneracy - the so-called Jahn-Teller (JT) systems. Orbital degrees of freedom and, in particular, their ordering or the cooperative Jahn-Teller effect, give rise to a very rich physics [1, 2]. The interplay between orbitals and spins often leads to rather peculiar magnetic structures, turning e.g. cubic perovskites like KCuF_3 into quasi-one-dimensional spin-chain materials [1]. It was recently suggested that in some JT systems orbitals remain disordered at all temperatures, forming an orbital liquid state [3, 4, 5, 6]. The suppression of an orbital ordering was discussed for materials with a simple cubic structure, e.g. the perovskite LaTiO_3 , and was attributed to a strong anisotropy of orbital interactions and a strong coupling between orbital and spin excitations. One would expect to find an even stronger tendency to form an orbital liquid in JT compounds with more complicated crystal structures, especially, in ‘geometrically frustrated’ systems [7], e.g. the spinel ZnMn_2O_4 , in which Mn^{3+} ions with the configuration $(t_{2g}^3 e_g^1)$ form a pyrochlore lattice of corner sharing tetrahedra, or the layered materials LiNiO_2 and NaNiO_2 with a triangular lattice of low-spin Ni^{3+} ion in the $(t_{2g}^6 e_g^1)$ configuration. Orbital ordering in such systems is an open issue, interesting from both theoretical and practical points of view, as some of these compounds (LiNiO_2 , NaNiO_2) are now studied as promising materials for rechargeable batteries, and their performance may be significantly affected by the JT effect.

An important difference between the TM oxides with ‘frustrated lattices’ and perovskites is the angle between the oxygen-metal bonds connecting two neighboring TM ions. While in perovskites this angle is close to 180° , in the geometrically frustrated JT systems it is typically 90° . Though usually ignored, this difference has important consequences for orbital and magnetic orderings. In this Letter we derive the Hamiltonian of the 90° -exchange and show that, unlike in perovskites, in frustrated JT

systems orbitals and spins are essentially decoupled and that orbital and magnetic orderings can be considered separately from each other. Considering in particular layered materials with a triangular lattice, we show that the orbital interactions are strongly frustrated, which results in a large number of disordered mean-field ground states. However, we argue that this frustration is lifted by quantum orbital fluctuations that stabilize a ferro-orbital state and induce a gap in the spectrum of orbital excitations. We also show that the ordering of spins in the layers is ferromagnetic. These results agree with experimental properties of NaNiO_2 [8] and lead us to a conclusion that the puzzling absence of both spin and orbital ordering in LiNiO_2 [9, 10] results from disorder rather than from the superexchange.

We first obtain the exchange Hamiltonian describing interactions between TM ions with one electron or hole on doubly degenerate e_g -levels. In this case orbital states are conveniently described by introducing isospins (or pseudospins) \mathbf{T}_j on each TM site j , which act on the up and down states, $|T^z = \pm \frac{1}{2}\rangle$ identified with, respectively, $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals. Quite generally, an effective interaction between the orbitals and spins on pairs of neighboring TM sites i and j has the form [1]

$$H_{ST} = \sum_{ij} [J_S(\mathbf{S}_i \mathbf{S}_j) + J_T T_i T_j + J_{ST}(\mathbf{S}_i \mathbf{S}_j) T_i T_j] \quad (1)$$

(for simplicity, we do not show here the full structure of the orbital interactions, which are strongly anisotropic both in real and isospin space). In perovskites with the 180° -bonds the spin- and orbital-exchange constants J_S and J_T , as well as the constant J_{ST} , describing the coupling between orbitals and spins, are all of the same order of magnitude. This makes the spin and orbital orderings dependent on each other [1]. The strong interplay between orbitals and spins is also crucial for the mechanisms of suppression of these orderings used in

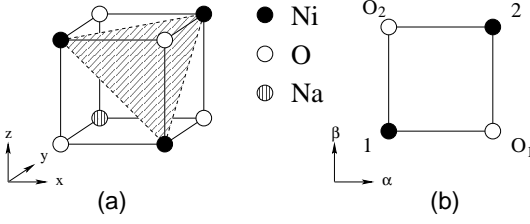


FIG. 1: The crystal structure of NaNiO_2 (a) and a plaquette in the $\alpha\beta$ -plane ($\alpha, \beta = x, y, z$) formed by two nearest-neighbor Ni ions, 1 and 2, and two oxygens, O_1 and O_2 (b).

Refs. [4, 11, 12] to explain an apparent absence of both orbital and magnetic ordering in LiNiO_2 [9, 10]. In particular, in the $SU(4)$ version of the model Eq.(1) [11, 12] both the spin and orbital interactions are isotropic and $J_S = J_T = \frac{1}{4}J_{ST}$. We first show that the actual situation in the 90° -systems is quite different: the orbital exchange is strongly anisotropic and $J_S \ll J_{ST} \ll J_T$.

We derive the exchange Hamiltonian using as an example the layered material NaNiO_2 , in which Ni and Na ions occupy consecutive [111]-planes of the NaCl structure (see Fig. 1(a)). In each plane the low-spin Ni^{3+} ions with one electron on the doubly degenerate e_g level form a triangular lattice. The exchange between two nearest-neighbor Ni ions in the planes occurs via common oxygens and the angle between the two oxygen p -orbitals involved in this exchange is 90° . The exchange between Ni ions from two neighboring planes (separated by a plane of Na ions) is weak and will be neglected here.

The electron hopping in the z -direction can only occur between the p_z oxygen and the $d_{3z^2-r^2}$ nickel orbitals. The corresponding hopping amplitude is denoted by t . All other processes are forbidden by symmetries of the oxygen p and nickel e_g orbitals. Thus, the hopping amplitude in the z -direction is t for the $|T^z = +\frac{1}{2}\rangle$ nickel state, and 0 for the $|T^z = -\frac{1}{2}\rangle$ state. More generally, the hopping in the α -direction ($\alpha = x, y, z$) is only nonzero for the oxygen p_α and the nickel $d_{3\alpha^2-r^2}$ orbitals. It is convenient to introduce the isospin operators $I^\alpha = \mathbf{T} \cdot \mathbf{n}^\alpha$, where \mathbf{n}^α are three unit vectors in the (T^x, T^z) plane

$$\mathbf{n}^x = -\frac{1}{2}\hat{\mathbf{z}} - \frac{\sqrt{3}}{2}\hat{\mathbf{x}}, \quad \mathbf{n}^y = -\frac{1}{2}\hat{\mathbf{z}} + \frac{\sqrt{3}}{2}\hat{\mathbf{x}}, \quad \mathbf{n}^z = \hat{\mathbf{z}}. \quad (2)$$

The operators I^x and I^y play the role of T^z for the x and y -directions, i.e. they describe the occupation of, respectively, the $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbital. The hopping amplitude in the α -direction is then t for the $|I^\alpha = +\frac{1}{2}\rangle$ state and 0 for the $|I^\alpha = -\frac{1}{2}\rangle$ state.

Figure 1(b) shows a plaquette in the $\alpha\beta$ -plane ($\alpha, \beta = x, y, z$) formed by two neighboring Ni sites 1 and 2 and the two oxygens shared by the oxygen octahedra surrounding the TM ions. An effective exchange Hamiltonian for two e_g nickel electrons is obtained by expanding the plaquette energy in powers of the hopping amplitude

t , which is assumed to be much smaller than the energy Δ of the electron transfer from O to Ni and the Hubbard repulsion on oxygen U_p . The orbital and spin exchange appears in the fourth order of the perturbative expansion and the higher-order terms are neglected here.

We first neglect also the Hund's rule coupling between the spins of two holes on oxygens. In that case the 90° -exchange is independent of a spin configuration and only involves orbitals. The orbital exchange Hamiltonian of the plaquette in the $\alpha\beta$ -plane has the form

$$H_T = J_T \mathcal{I}^{\alpha\beta} + \text{const}, \quad (3)$$

where

$$\mathcal{I}^{\alpha\beta} = \left(\frac{3}{2} - I_1^\alpha\right) \left(\frac{3}{2} - I_2^\beta\right) + \left(\frac{3}{2} - I_1^\beta\right) \left(\frac{3}{2} - I_2^\alpha\right) \quad (4)$$

and J_T is the coupling constant specified below. The factor $\frac{3}{2} - I_1^\alpha$ counts the number of the oxygen electrons that can hop to the Ni site 1 along the bond in the α -direction. This number equals 1, if the e_g -electron is in the state $|I_1^\alpha = +\frac{1}{2}\rangle$, and 2, if the electron occupies the state $|I_1^\alpha = -\frac{1}{2}\rangle$. (For one hole on e_g -level, as in Cu^{2+} , the exchange interaction corresponding to Eq.(4) involves combinations $(\frac{1}{2} + I^\alpha)$ instead of $(\frac{3}{2} - I^\alpha)$.) The two terms in Eq.(4) correspond to the two exchange paths on the plaquette through the oxygens O_1 and O_2 .

The orbital coupling

$$J_T = -\frac{4t^2}{\Delta^2(2\Delta + U_p)} + \frac{2t^4}{\Delta^3} = \frac{2t^4 U_p}{\Delta^3(2\Delta + U_p)} \quad (5)$$

is the sum of the contributions of two different mechanisms of the orbital exchange. The first term in Eq.(5) is due to the exchange via the intermediate states with two holes on one of the oxygens from the plaquette. The mechanism resulting in the second term in Eq.(5) works even for infinite U_p , when the two-hole oxygen states are forbidden. To understand its origin consider first a single Ni site inside the oxygen octahedron. The hopping of electrons from the 6 oxygens to nickel results in the energy decrease δE . For two neighboring Ni sites this decrease is smaller than $2\delta E$, as the surrounding octahedra share two oxygens and the two-hole oxygen states are forbidden for infinite U_p . The effect of the blocking of the two-hole states on common oxygens depends on orbital states of the e_g -electrons, which gives rise to the orbital exchange with the coupling constant $\frac{2t^4}{\Delta^3}$.

The intermediate states with two holes on one oxygen also result in a spin exchange. As in such states the holes occupy two mutually orthogonal orbitals p_α and p_β , the spin exchange is only possible due to the Hund's rule coupling J_H between the spins of the holes (in systems with the 180° -bonds the spin exchange occurs even for $J_H = 0$). The corresponding exchange Hamiltonian involves both spin and isospin operators and to the lowest-

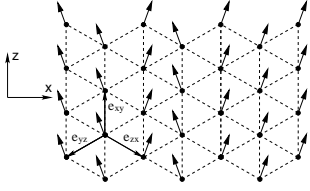


FIG. 2: The triangular lattice formed by Ni ions in the [111]-plane. Shown also is a disordered mean-field ground state, in which the isospins form lines parallel to the unit vector \mathbf{e}_{xy} , such that $\langle T_j^z \rangle$ is the same on all lattice sites, while the sign of $\langle T_j^x \rangle$ varies arbitrary from line to line.

order in powers of J_H it has the form

$$H_{TS} = -J_{TS} \mathcal{I}^{\alpha\beta} \left[\frac{3}{4} + (\mathbf{S}_1 \mathbf{S}_2) \right], \quad (6)$$

where $J_{TS} = \frac{4t^4 J_H}{\Delta^2 (2\Delta + U_p)^2}$ and $\mathcal{I}^{\alpha\beta}$ is given by Eq.(4). The interaction described by Eq.(6) is different the 180° -exchange in two important respects. First, since for any orbital state the expectation value $\langle \mathcal{I}^{\alpha\beta} \rangle > 0$, the spin exchange is effectively ferromagnetic independent of an orbital state (the average spin-exchange coupling $-J_{TS} \langle \mathcal{I}^{\alpha\beta} \rangle < 0$ is negative). Second, since $J_H \ll U_p$, the spin-isospin coupling in the 90° -systems is weaker than the pure orbital exchange, described by Eq.(3):

$$\frac{J_{TS}}{J_T} = \frac{J_H}{U_p} \frac{2\Delta}{(2\Delta + U_p)}.$$

Thus, in 90° -exchange systems spins and orbitals cannot strongly influence each other, i.e. they are essentially decoupled. (A similar conclusion was reached by Reitsma and Feiner (unpublished). We are grateful to L. F. Feiner for informing us about their results.)

We can now obtain the Hamiltonian describing the orbital interactions in the Ni layers of NaNiO_2 (see Fig. 1a). In each layer Ni ions form a triangular lattice, the sites of which lie on intersections of the three sets of lines parallel to the unit vectors \mathbf{e}_{xy} , \mathbf{e}_{yz} , and \mathbf{e}_{zx} , as shown in Fig. 2. It will be convenient to identify $\mathbf{e}_{\alpha\beta}$ with the three unit vectors in the isospace (see Eq.(2)) by $\mathbf{n}^x = \mathbf{e}_{yz}$, $\mathbf{n}^y = \mathbf{e}_{zx}$, and $\mathbf{n}^z = \mathbf{e}_{xy}$. The bonds between the nearest-neighbor sites j and $j + \mathbf{e}_{\alpha\beta}$ of the triangular lattice (the lattice constant is put to 1) are diagonals of the Ni-O plaquettes lying in the $\alpha\beta$ plane (cf. Fig. 1b). Hence, the Hamiltonian, describing orbital interactions on the triangular lattice has the form:

$$H_T = J_T \sum_j \sum_{\substack{\alpha\beta \\ \alpha \neq \beta}} I_j^\alpha I_{j+\mathbf{e}_{\alpha\beta}}^\beta. \quad (7)$$

The terms linear in the operators I_j^α (see Eq.(3)) are canceled in (7), since $\sum_\alpha I_j^\alpha = 0$.

The Hamiltonian Eq.(7) is invariant under the global rotation of the isospin operators T^α over the angle $\frac{2\pi}{3}$

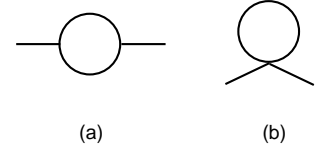


FIG. 3: The self-energy diagrams due to the cubic (a) and the quartic (b) interactions that result in a gap opening and a two-dimensional dispersion.

around the y -axis combined with the rotation of the triangular lattice over the same angle. This transformation is equivalent to a cyclic permutation of the indices x , y , and z of the vectors $\mathbf{e}_{\alpha\beta}$ and the isospin operators I^α . Thus the Hamiltonian Eq.(7) has the same symmetry as the so-called ‘compass’ model, describing exchange interactions between TM ions on a cubic lattice [1, 13] (note, however, that in our case the three operators I^x , I^y , and I^z are not independent).

The orbital exchange on a triangular lattice turns out to be strongly frustrated and the mean-field ground state is not unique. The simplest states with the minimal energy $E_0 = -\frac{3}{8}J$ per site are ferro-orbital states, in which $\langle \mathbf{T}_j \rangle = T\mathbf{m}$ on all lattice sites, where \mathbf{m} is an arbitrary unit vector in the (T^x, T^z) -plane and $T = \frac{1}{2}$. The energy of these states is independent of orientation of \mathbf{m} , even though the Hamiltonian (7) is not invariant under arbitrary rotations in the (T^x, T^z) -plane (this continuous ground-state degeneracy is similar to the one of the ‘compass’ model [13]). Furthermore, there exist also disordered mean-field ground states, which can be obtained from the ferro-orbital states by inverting the sign of $\langle T_j^x \rangle$ on an arbitrarily selected set of lines parallel to \mathbf{e}_{xy} (see Fig. 2). Such states are ordered along the xy -lines, but there are no long-range correlations between the x -projections of isospins in the transverse direction. By circular permutations of the x , y , and z indices one can obtain similar states, which are only ordered along the lines parallel to the \mathbf{e}_{yz} and \mathbf{e}_{zx} vectors.

This large ground-state degeneracy is lifted by quantum orbital fluctuations (the so-called ‘order-from-disorder’ mechanism [14, 15]). First, we have checked numerically that disordered states (see Fig. 2) have a higher energy of the zero-point fluctuations than the corresponding uniform states. Second, the zero-point energy of uniform states has 6 minima at the isospin orientations $\mathbf{m} = \pm \mathbf{n}^x, \pm \mathbf{n}^y, \pm \mathbf{n}^z$. In the original notation these are the ferro-orbital states with one of the orbitals $d_{3z^2-r^2}$, $d_{3x^2-r^2}$, $d_{3y^2-r^2}$, $d_{x^2-y^2}$, $d_{y^2-z^2}$, and $d_{z^2-x^2}$ occupied at each site. Furthermore, the anharmonicity effects [16] usually stabilize elongated octahedra, i.e. the orbitals $d_{3z^2-r^2}$, $d_{3x^2-r^2}$, or $d_{3y^2-r^2}$. As was mentioned above, spins in layers order ferromagnetically.

We would like to point out that the standard description of orbital excitations with non-interacting bosons (‘isospin-wave approximation’) is insufficient for the cal-

ulation of quantum corrections to the ground-state energy of the frustrated Hamiltonian Eq.(7). In this approximation the orbital excitation spectrum for the six ground states is one-dimensional

$$\omega_{\mathbf{q}} = 3\sqrt{2}TJ_T \left| \sin \frac{(\mathbf{q} \cdot \mathbf{m})}{2} \right|, \quad (8)$$

which is a direct consequence of the absence of long-range correlations between chains in disordered mean-field ground states. The gapless one-dimensional spectrum leads to infrared-divergent fluctuations. To get rid of them, one has to take into account interactions between the bosons, which can be consistently done in the large isospin limit, $T \gg 1$. The interactions suppress quantum fluctuations by opening a gap and inducing a dispersion in the direction transverse to \mathbf{m} . This can be understood from the fact that the self-energy diagrams, shown in Fig. 3 (a) and (b), diverge unless a gap is introduced (in field theory a similar mechanism is known as a ‘dynamical mass generation’ [17]). The physical origin of the gap is the breaking of the continuous ground-state degeneracy by quantum fluctuations [13]. In the large- T limit the quantum fluctuations are relatively small and the gap $\Delta \propto J_T\sqrt{T}$ is much smaller than the band width $W \sim 3\sqrt{2}J_T T$ of the orbital excitations. The dispersion in the transverse direction is of the order of Δ [18].

The main conclusions of our theory of the exchange in frustrated systems (spins are coupled much weaker than orbitals, the ground state is ordered both ferro-orbitally and ferromagnetically) are in agreement with the orbital and magnetic structure of the layered compound NaNiO_2 , which undergoes two transitions: At $T_o = 480\text{K}$ the oxygen octahedra become elongated, which corresponds to the ferro-orbital ordering of the $d_{3z^2-r^2}$ -type, and at the much lower temperature, $T_s = 20\text{K}$, the Ni spins in the [111] layers order ferromagnetically [8].

It is, therefore, very puzzling that the structurally identical material LiNiO_2 shows neither orbital nor spin ordering. In principle, we cannot exclude that the quantum orbital fluctuations, which for $T = \frac{1}{2}$ are relatively large, destroy the long-range ferro-orbital ordering and stabilize an orbital liquid (such quantum melting of the ‘order-from-disorder’ was discussed in the context of another frustrated system in Ref. [19]). Since for $T = \frac{1}{2}$ there is no small parameter in the problem, the question whether the ground state of the orbital Hamiltonian Eq.(7) is ordered or disordered, can only be resolved by numerical calculations that are beyond the scope of this Letter. In any case, this possible explanation of the absence of orbital ordering in LiNiO_2 is fundamentally different from those based on a strong interplay between orbitals and spins [4, 11, 12]. Actually, due to the decoupling of spins from orbitals in frustrated systems, an orbital liquid should still have a ferromagnetic order.

We think that the puzzles surrounding LiNiO_2 indicate an importance of electron-lattice interactions and disorder,

not included in the present theory. As was argued in Refs. [8, 20], the ‘intrinsic’ disorder caused by the presence of magnetic Ni ions in the Li [111] planes, results in a strong interlayer coupling that frustrates the ferromagnetic spin ordering in Ni layers. In NaNiO_2 such disorder should be weaker: as the size difference of Na and Ni ions is larger than that of Li and Ni ions, the alternating stacking of the Na and Ni [111] layers is more perfect than that of Li and Ni in LiNiO_2 . The larger charge radius of the Na ion also implies stronger electron-lattice interactions in NaNiO_2 . In general, such interactions suppress quantum orbital fluctuations and stabilize a ferro-orbital ordering [21, 22]. This may explain why NaNiO_2 is orbitally ordered, while LiNiO_2 is not.

In conclusion, we developed a theory of the orbital and spin exchange in JT systems with doubly degenerate electronic orbitals and 90° metal-oxygen-metal bonds. We showed that in these systems spins and orbitals are essentially decoupled: spins interact much weaker than orbitals and the spin exchange is ferromagnetic for any orbital state. The orbital exchange between TM ions on a triangular lattice is strongly frustrated, resulting in infinite number of disordered classical ground states. An even stronger frustration can be shown to occur in spinels, in which TM ions form a pyrochlore lattice (to be published elsewhere). We showed, however, that small quantum orbital fluctuations remove the frustration and induce a ferro-orbital ordering. Our theory is in agreement with the orbital and magnetic structure observed in NaNiO_2 . We also argued that large quantum fluctuations and ‘intrinsic’ disorder may, in principle, turn a frustrated system into an orbital liquid, which may explain the absence of orbital ordering in LiNiO_2 .

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- [1] K. I. Kugel and D. I. Khomskii, Sov. Phys. JETP **52**, 501 (1981); Sov. Phys. Uspekhi **25**, 232 (1982).
 - [2] Y. Tokura and N. Nagaosa, Science, **5465**, 462 (2000).
 - [3] S. Ishihara, M. Yamanaka, and N. Nagaosa, Phys. Rev. B **56**, 686 (1997).
 - [4] L. F. Feiner, A. M. Oles, and J. Zaanen, Phys. Rev. Lett. **78**, 2799 (1997).
 - [5] B. Keimer *et al.* Phys. Rev. Lett. **85**, 3946 (2000).
 - [6] G. Khaliullin and S. Maekawa, Phys. Rev. Lett. **85**, 3950 (2000).
 - [7] A. P. Ramirez, C. L. Broholm, R. J. Cava, and G. R. Kowach, Physica B **280**, 290 (2000) and references therein.
 - [8] E. Chappel *et al.*, Eur. Phys. J. B **17**, 609 (2000).
 - [9] Y. Kitaoka *et al.*, J. Phys. Soc. Jap. **67**, 3703 (1998).
 - [10] F. Reynaud *et al.*, Phys. Rev. Lett. **86**, 3638 (2001).
 - [11] Y. Q. Li, M. Ma, D. N. Shi, and F. C. Zhang, Phys. Rev.

- Lett. **81** 3527 (1998).
- [12] M. van der Bossche, P. Azaria, P. Lecheminant, and F. Mila, Eur. Phys. J. B **17**, 367 (2000).
 - [13] G. Khaliullin, Phys. Rev. B **64** 212405 (2001).
 - [14] J. Villain, R. Bidaux, J. P. Carton, and R. Conte, J. de Physique **41**, 1263 (1980).
 - [15] E. F. Shender, Sov. Phys. JETP **56**, 178 (1982).
 - [16] D. I. Khomskii and J. van der Brink, Phys. Rev. Lett. **85**, 3329 (2000).
 - [17] S. Coleman and E. Weinberg, Phys. Rev. D **7**, 1888 (1973).
 - [18] Details of the calculation of the dispersion of orbital excitations, which also requires a vertex renormalization, will be published elsewhere.
 - [19] P. Lecheminant *et al.*, Phys. Rev. B **56**, 2521 (1997).
 - [20] D. Mertz *et al.*, Phys. Rev. B **61**, 1240 (2000).
 - [21] J. Kanamori, J. Appl. Phys., **31**, 14S (1960).
 - [22] R. Englman and B. Halperin, Phys. Rev. B **2**, 75 (1970).